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# Canadian Patent Office

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Patent No. 597,473

## Process for the Manufacture of Phosphorus-Containing Polyesters and Copolymers Thereof

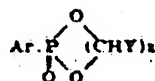
Werner Starck, Herbert Vilcek and Jakob Winter, Hofheim/Taunus, Germany, and Fritz Kochlitz, Frankfurt/Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt/Main, Germany

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3 Claims—No drawing

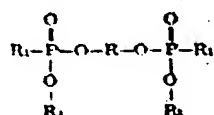
The present invention relates to new phosphorus-containing polyesters and to a process for their manufacture. It furthermore relates to copolymers of said polyesters.

It is known to prepare well defined monomeric cyclic esters of the formula



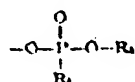
wherein X stands for 2 or 3 and Y represents hydrogen or an alkyl radical by reacting phenylphosphonic acid dichloride at 25°C. or lower temperatures with corresponding glycols. If desired in the presence of hydrogen halide acceptors. The products thus obtained are, in most cases, soluble in water and sometimes crystallized compounds.

Furthermore there are known low molecular glycolic esters of phosphonic acids, for example compounds of the formula



wherein R represents the carbon radical of the glycol and R<sub>1</sub> a hydrocarbon radical which may be substituted to a small degree by chlorine, bromine, alkoxy and nitro groups.

Now we have found that phosphorus-containing polyesters containing a plurality of the group

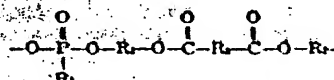


wherein R<sub>1</sub> stands for alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, alkylaryl and derivatives of these groups and R<sub>2</sub> stands for a bivalent organic group, can be prepared by reacting functional derivatives of phosphonic acids with polyhydric alcohols which may be saturated or may have olefinic double bonds or with mixtures thereof. When correspondingly choosing the components and the proportions thereof, products are obtained which are extremely viscous, insoluble in water and which have no tendency to crystallize.

The above-mentioned polyesters can be modified by partially replacing a phosphonate radical in the polyphosphonates by carboxylic acid radicals

thus obtaining likewise new, phosphorus-containing polyesters of polyhydric alcohols. The fundamental feature of said polyesters is the phosphonate radical built in in an ester-like manner.

In the case of dicarboxylic acids the new compounds contain a plurality of the group



wherein R<sub>1</sub> stands for alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, alkylaryl and derivatives of these groups and R<sub>2</sub> and R<sub>3</sub> each for a bivalent organic group.

As derivatives of phosphonic acids there may be used, for example, phosphonic acid dihalides, preferably phosphonic acid dichlorides, and phosphonates, such as methyl, ethyl, propyl, allyl, chloroethyl esters having the radical R<sub>1</sub> directly bound to the phosphorus.

The radical R<sub>1</sub> may stand, for example, for alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl and alkylaryl as well as for hydrocarbon radicals of this kind substituted by halogen, hydroxyl, alkoxy and in the case of aromatic radicals, by nitro and/or amino groups.

Consequently there may be used, for example, methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, dodecyl, stearyl, oleyl, butenyl, propenyl, vinyl, cyclopentyl, methylcyclohexyl, ethylcyclohexyl, cyclohexenyl, cyclopentenyl, cyclopentadienyl, endomethylen-cyclohexyl, phenyl, methylphenyl, dimethylphenyl, ethylphenyl, isopropylphenyl, methyl-isopropylphenyl, benzyl, cinnamyl, chloromethyl, dichloromethyl, trichloromethyl, bromomethyl, trifluoromethyl, β-chloroethyl, chlorobutyl, chlorophenyl, bromophenyl, trifluoromethylphenyl, nitrophenyl, aminophenyl, anisyl, phenetyl, hydroxyphenyl, cresyl, chlorocresyl or oxethyl.

The polyphosphonates (polyesters of phosphonic acid) can be prepared, for example, in a manner, such that the dibromides or diiodides, preferably, however, the dichlorides of the phosphonic acids described, are allowed to act upon the polyhydric alcohols at temperatures above +25°C., preferably between 40 and 100°C. Higher temperatures up to about 200°C. may likewise be applied. Advantageously the reaction is started at comparatively low temperatures, e.g. at about 25°C.; the temperature is then raised slowly in order to avoid a too vigorous evolution of hydrogen chloride. The hydrogen halide set free in the course of the reaction can be eliminated by the application of reduced pressure, by passing through an inert gas current or, if desired, by suitable hydrogen halide acceptors, such as tertiary amines, for example triethylamine, dimethylaniline, by the addition of metals binding hydrogen halide, such as zinc, aluminum, iron etc. or by merely increasing the temperature.

Another way for the manufacture of the polyphosphonates consists in re-esterifying phosphonates of monohydric, preferably easily volatile alcohols with polyhydric alcohols. Said re-esterifications can advantageously be carried out at temperatures above 100°C. with addition of known acid or basic re-esterification catalysts under atmospheric or reduced pressure. It is expedient continuously to remove from the reaction mixture

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the monohydric alcohol which is set free, generally by means of a distillation. In re-esterification of this kind there may be used as catalysts, for example, paratoluene-sulfonic acid or the esters thereof, hydrogen chloride, sulfuric acid, paratoluene-sulfochloride, cadmium acetate, sodium acetate, sodium methylate, potassium ethylate, lithium hydride, zinc oxide, lead oxide, calcium oxide or magnesium oxide.

Mixed polyesters having phosphonate and carboxylate fractions within the same ester chain can be prepared in a similar manner. On principle it is possible to use as starting material preformed pure polymeric phosphonates and polymeric carboxylates. It is more advantageous, however, to carry out the condensation of the mixed polyesters from the onset in mixtures of the starting materials. Thus, when using the phosphonates of monohydric alcohols, it is possible to react them from the beginning, in addition to esters, for example corresponding esters of carboxylic acids, with the polyhydric alcohols. It is likewise possible simultaneously to react polyhydric alcohols with phosphonic acid dihalides and esters of di- or polycarboxylic acids and monohydric alcohols, while the hydrogen chloride formed acts additionally as re-esterification catalyst.

Moreover, it is possible to react the two kinds of acid one after the other. There can be first prepared a pure polyester, for example, a polyphosphonate, if desired with high molecular weight, and the carboxylic acid and further amounts of polyhydric alcohol can be subsequently added, or short chain precondensates can be formed. In the latter case there can be added from the outset an excess amount of polyhydric alcohol, if desired almost the entire amount required for the formation of the mixed polyester.

In all these reactions there can be used instead of carboxylic acids the anhydrides thereof, as far as they exist, or other reactive derivatives, such as, for example, their esters, chlorides or bromides. The esterification or re-esterification is carried out according to known methods. The water which is formed in the course of the reaction may be eliminated by means of an inert gas current bubbling through the reaction mixture or with the aid of an entrainer. Generally temperatures between 100 and 220°C. are required for this purpose and at the end of the reaction in most cases still higher temperatures up to about 260°C. As re-esterification catalysts there may be used the above-mentioned compounds.

As carboxylic acids there come into consideration preferably polybasic acids having at least one carbon atom between the carboxylic groups. There are used, for example, malonic acid, succinic acid, chlorosuccinic acid, adipic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, hexachloroendomethylenehydriphthalic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, malic acid, tartaric acid, trimelic acid, tricarballic acid, aconitic acid, citric acid, hemimellitic acid or pyromellitic acid.

As already indicated above, there may be used in addition to the di- or polycarboxylic acids mentioned or in addition to the phosphonic acid derivatives monobasic carboxylic acids, such as saturated or unsaturated aliphatic (having at least 2 carbon atoms) or cycloaliphatic as well as aromatic or heterocyclic carboxylic acids or hydroxy acids or carboxylic acids substituted by halogen, for example, acetic acid, propionic acid, butyric acid, crotonic acid, sorbic acid, benzoic acid, chloro-

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benzoic acid, furencarboxylic acid, furfuracrylic acid, cinnamic acid, nicotinic acid, lactic acid, hydroxybutyric acid, chloroacetic acid, chlorobutyric acid, or bromobenzoic acid.

The number of suitable polyhydric alcohols is, of course, extremely large. There are mentioned, for example, ethylene glycol, polyglycol ethers having, for example, 6 molecules of ethylene oxide obtainable e.g. by polymerization of ethylene oxide, propylene glycol, poly-propylene glycol, butylene glycol, hexane-diol, butenediol, pinacol, mono- and polycyclic alcohols, for example tricyclodecanedi- or trimethylol, glycerol, hexane-triol, trimethylol-propane, pentaerythrite, dipentaerythrite, sorbitol, 1,2-diphenylethylene glycol, phthalyl alcohol, or partial alkyl ethers of the aforementioned tri- or polyhydric alcohols containing at least 2 free OH groups. Especially suitable are polyhydric alcohols containing between the hydroxy groups not more than 3 carbon atoms. In many cases it is advantageous to replace part of the polyhydric alcohols by saturated or unsaturated mono-hydric alcohols or to combine at least trihydric alcohols with monohydric alcohols. In this case, too, halogen-containing derivatives are included.

As monohydric alcohols there come into consideration, for example, methyl, ethyl, propyl, butyl alcohol, ethyl-hexanol, allyl alcohol, oleyl alcohol, or chlorethanol. The amounts of the monohydric alcohols used preponderantly depend on the at least trivalent alcohol used. The amounts of monocarboxylic acids used are likewise determined by the at least trivalent alcohols. When using a polyhydric alcohol, for example sorbitol, up to 4 mols of a monohydric alcohol can be employed per mol of sorbitol in case equimolecular amounts of dicarboxylic acid are used. In this case only slightly cross-linked products can be obtained; if, however, polyhydric alcohols are reacted in the absence of monohydric alcohols, highly cross-linked products can be obtained. Also when varying the amounts of monohydric alcohol and tri- or polyhydric alcohols the solubility of the formed polyester can be modified as desired and more or less cross-linked products can be obtained. When using tri- or polyhydric alcohols, for example, sorbitol, up to 4 hydroxyl groups can be esterified by monovalent carboxylic acids and in this manner, too, the solubility, the degree of cross-linking and other properties, of the polyester formed can be modified as desired. Polyesters of phosphonic acid derivatives and di- or polyhydric alcohols containing no carboxylic acids can be prepared in a similar manner as described above for polyesters of carboxylic acids and phosphonates on the one hand and di- or polyhydric alcohols on the other hand. Thus products can be prepared which still contain free hydroxylic groups or free carboxylic groups.

When preparing polyphosphonates modified by poly-carboxylic acids, it is expedient in general to choose the proportion of the phosphonic acid to the sum of the carboxylic acids between 1:10 and 10:1. It is possible, however, as shown in the examples, to dispense with the addition of carboxylic acids or to add less than 10% of carboxylic acids. On the other hand it is possible to operate with a smaller ratio of phosphonic acid to carboxylic acid than 1:10; in some cases, for example, there can be prepared products containing about 5% of phosphonic acid, calculated on the sum of the carboxylic acids.

In case the products prepared according to the process of the invention still contain double bonds, which is the fact, for example, when using con-

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comitantly maleic acid, fumaric acid, allyl alcohol, crotonic acid, vinyl-phosphonate radicals or other unsaturated compounds, the properties of the resins can be further varied by polymerization of said products, for example, in the presence of known polymerization catalysts, such as peroxides, for example, benzoyl peroxide, or lauryl peroxide. Thus, there are obtained soft to hard polymers which are incombustible or self-extinguishing.

On the other hand thermo-hardenable resins can be obtained in case the polyesters are preponderantly prepared from tri- and/or polyhydric alcohols.

The polyphosphonates obtainable according to the process of the invention and the mixed polyesters of phosphonic acids and carboxylic acids are resinous products which, in most cases, have high molecular weights and which are well soluble in various organic solvents as far as they are not cross-linked. Especially important are their self-extinguishing properties or their non-combustibility owing to the content of phosphorus, which properties can distinctly be recognized already when only a small portion of the acids incorporated by condensation consists of phosphonic acids. The products according to the invention possess self-extinguishing properties when containing only 1% by weight of phosphorus. Products of this kind are suitable for the most part as flame-proof additives to a number of substances, for the impregnation of paper and textile materials, glass fibers and the like, as adhesives and lacquers, paints and as intermediate products and starting materials for the preparation of plastic materials. When accordingly choosing the esterification components excellent fire-proof baking lacquers are obtained. The products obtained by subsequent polymerization are especially suitable as plastic materials.

It has, furthermore, been found that the molecular weight of the polyesters prepared according to the process of the present invention which contain unsaturated groups can be likewise increased when said polyesters are copolymerized under known conditions with low molecular compounds containing activated double bonds.

Activated double bonds are those which stand in neighbouring position to either a functional group, such as the hydroxymethyl, carboxyl or nitrile group, or to aromatic nuclei or to phosphorus. The hydroxy and carboxylic groups may be free or esterified.

As examples for low molecular compounds there are mentioned among others styrene, alkylated styrenes, vinylnaphthalene, vinyl esters, such as vinyl acetate, acrylic acid and methacrylic acid and the esters and nitriles thereof, allyl and methallyl esters of saturated or unsaturated mono- and polycarboxylic acids, allyl and methallyl carbonates, allyl and methallyl phosphates and phosphonates, esters of vinylphosphonic acid, triallylcyanurate, triallyltrimellitate, unsaturated polyesters of low molecular weight, especially polyesters containing allyl or methallyl ester groups and the derivatives thereof, especially in case they are substituted by halogen.

It is suitable to admix the unsaturated monomers with the unsaturated phosphorus-containing polyesters in a proportion, such that the monomer represents about 10 to 60%, preferably 20-40%, of the total amount.

The products obtained according to the invention are distinguished by their insolubility in organic solvents. They can only be swollen in said solvents.

The products are completely transparent, and have a low and constant content of phosphorus.

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they are incombustible or possess self-extinguishing properties. Consequently they are suitable for many applications, for example, for the manufacture of shaped articles, for the impregnation of paper and textile materials and as lacquers and paints for surface protection. Moreover, they can be admixed with various additives, for example highly chlorinated hydrocarbons, fillers of organic or inorganic nature etc. and they can be improved by embedding organic or inorganic fibers, for example, glass fibers.

The polymerization takes place by irradiation and/or by heating and/or by addition of activators at normal or elevated temperature. As activators there may be used peroxides, for example benzoyl peroxide, tert-butyl hydroperoxide, cumenehydroperoxide, toluene peroxide, di-tert-butyl peroxide, chlorobenzoyl peroxide, lauryl peroxide, or azo-diiso-acrylonitriles, such as azo-diiso-butronitrile, sulfonic acids, such as para-methoxysulfonic acid, dodecylsulfonic acid, cyclohexylsulfonic acid, benzenesulfonic acid, para-toluene-sulfonic acid or sulfonamides, such as N-bis-(para-tolylsulfonmethyl)-methylamine, N-para-tolylsulfonmethyl-2-hydroxyethylamine, paratolylsulfoncarbinol, phenylsulfoncarbinol, para-tolylsulfonpropylcarbinol, or para-chlorophenylcarbinol.

Polymerizations of this kind are generally described in U.S. Patent 2,255,313 and the conditions mentioned in this publication can be applied also in the process according to our invention.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the parts being by weight unless otherwise stated, and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the liter:

#### Example 1

62 Parts of ethylene glycol (1 mol) are mixed dropwise at 60°C., with 195 parts of phenylphosphonic acid dichloride (1 mol) according to the reaction occurring and the heat effect evolved. The mixture is then heated for 6 hours under reduced pressure at 60°C. until free chlorine ions can no longer be detected in the reaction product. The reaction product obtained represents after cooling a completely clear, only slightly colored and highly viscous liquid, insoluble in cold and boiling water.

#### Example 2

105 Parts of diethylene glycol (1 mol) are mixed at 55-60°C. with 195 parts of phenylphosphonic acid dichloride (1 mol) according to the reaction occurring and the heat effect evolved, and the mixture is then maintained at about 60°C. under reduced pressure for approximately 5 hours. The reaction mixture is then heated for some time under reduced pressure at 160°C. in order to eliminate residues of free hydrogen chloride still present. A highly viscous, only slightly colored and completely clear product is obtained which is free of chlorine ions and which is insoluble in cold and boiling water.

#### Example 3

150 Parts of triethylene glycol (1 mol) are mixed dropwise at 50-55°C. with 195 parts of phenylphosphonic acid dichloride (1 mol) and the mixture is then heated under reduced pressure for 3 hours at 55°C. In order to eliminate the last residues of free hydrogen chloride the mixture is then heated for some time up to 130°C. under reduced pressure. A highly viscous product is obtained which is free of chlorine and which is insoluble in cold and boiling water.

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## Example 4

106 Parts of diethylene glycol (1 mol) are mixed dropwise at 40-45°C. with 145 parts of vinylphosphonic acid dichloride (1 mol). The mixture is then maintained for 6 hours at 45°C. under reduced pressure. Residual amounts of free hydrogen chloride are eliminated by heating the mixture under reduced pressure to 100°C.

The highly viscous and clear reaction product obtained is insoluble in water. It can be converted by heating advantageously in the presence of peroxides, such as benzoyl peroxide, to an insoluble product.

## Example 5

106 Parts of diethylene glycol (1 mol) are mixed dropwise at 50-60°C. with 181.5 parts of  $\beta$ -chloroethanephosphonic acid dichloride (1 mol). The mixture is then heated for 2 hours at about 60°C. under reduced pressure. Residual amounts of free hydrogen chloride are eliminated by heating the mixture under reduced pressure to 120°C. The reaction product obtained is a highly viscous liquid which is insoluble in water.

## Example 6

82 Parts of ethylene glycol (1 mol) are mixed dropwise at 55-65°C. with 201 parts of cyclohexanephosphonic acid dichloride (1 mol). The mixture thus obtained is then maintained for 1-2 hours at 80°C. under reduced pressure. Residual amounts of hydrogen chloride can be eliminated by heating the mixture under reduced pressure at 160°C. The reaction product obtained is a highly viscous clear liquid which is insoluble in water.

## Example 7

62 Parts of ethylene glycol (1 mol) are mixed dropwise 55-60°C. with 189 parts of amylphosphonic acid dichloride (1 mol) and the mixture is maintained at that temperature for 2 hours under reduced pressure. Residual amounts of free hydrogen chloride still present can be eliminated by heating the mixture under reduced pressure to 165°C. A highly viscous liquid is obtained which is insoluble in water.

## Example 8

23 Parts of glycerol (0.25 mol), 60 parts of diethylene glycol (0.57 mol) and 10 parts of n-butanol (0.135 mol) are mixed dropwise at 60°C. with 200 parts of phenylphosphonic acid dichloride. The mixture is then heated for 6 hours under reduced pressure at about 60°C. The residual hydrogen chloride is eliminated by heating the mixture under reduced pressure to about 140°C. The reaction product is highly viscous and insoluble in water.

## Example 9

212 Parts of diethylene glycol (2 mols) are reacted at 60°C. with 195 parts of phenylphosphonic acid dichloride (1 mol) and the hydrogen chloride which is set free is eliminated from the reaction mixture, first at 60°C. and then completely at 160°C. 98 Parts of maleic anhydride (1 mol) and 50 parts by volume of xylene (as entrainer) are then added, the whole is heated under reflux and 18 parts by volume of water are drawn off in the course of about 20 hours, finally at 170°C. The entrainer is distilled off under reduced pressure and the reaction product is cooled after having been heated for about 1 hour to 180°C. A highly viscous, yellow and clear mass is obtained which does no longer flow in the cold. The product is

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soluble in esters and hydrocarbons and can be polymerized in the presence of benzoyl peroxide to obtain a clear resin which is non-combustible or has self-extinguishing properties.

## Example 10

219 Parts of diethylene glycol (2 mols) are reacted at 40-45°C. with 145 parts of vinylphosphonic acid dichloride (1 mol) and the hydrogen chloride set free is completely eliminated under reduced pressure, first at 45°C. and then at 100°C. To the reaction mixture are then added 98 parts of maleic anhydride (1 mol) and 50 parts by volume of xylene. After having installed a device for separating water, the mixture is heated under reflux. 17 Parts by volume of water are drawn off in the course of about 20 hours, finally at 175°C. The xylene is distilled off under reduced pressure and the reaction product is maintained for about 1 hour at 180°C. The reaction product is a highly viscous, slightly yellow mass which does no longer flow in the cold and which is soluble in hydrocarbons. When heated in the presence of peroxides polymerization occurs and non-combustible or self-extinguishing masses are obtained.

## Example 11

75 Parts of hexane-triol (0.56 mol) and 100 parts of phenylphosphonic acid dichloride (0.51 mol) are heated under reduced pressure, first at 60°C. and finally at 160°C. until chloride can no longer be detected in the reaction mixture. 17 Parts of ethylene glycol (0.27 mol), 48 parts of maleic anhydride (0.49 mol) and 30 parts by volume of xylene are then added, a device for separating water is installed and the mixture is heated under reflux. Within about 18 hours approximately 9 parts by volume of water can be drawn off while the temperature of the reaction mixture finally amounts to 190°C. The xylene is then distilled off under reduced pressure and the mixture is maintained for about another hour at 190°C.

The reaction product is a highly viscous mass which does no longer flow in the cold; it is soluble in esters and hydrocarbons and can be polymerized in the presence of peroxides.

## Example 12

368 Parts of a condensate from phenylphosphonic acid dichloride and ethylene glycol (molar ratio 1:1) are heated with 134 parts of hexane-triol (1 mol), 74 parts of butanol (1 mol) and 196 parts of maleic anhydride (2 mols). The butanol simultaneously serves as reaction component and as entrainer for the water formed. By means of a device for separating water 26 parts by volume of water are drawn off in the course of about 17 hours at a final temperature of 190°C. The reaction mixture is then kept under reduced pressure for 2 hours and subsequently allowed to cool. A highly viscous, slightly dark colored product is obtained.

## Example 13

144 Parts of maleic acid dimethyl ester (1 mol), 124 parts of ethylene glycol (2 mols) and 1.5 parts of CaO are heated together. After having terminated the separation of methanol, the mixture is cooled to +55°C. At that temperature 185 parts of phenylphosphonic acid dichloride (1 mol) are added dropwise to the mixture according to the reaction occurring. The hydrogen chloride set free is simultaneously eliminated under reduced pressure. When the evolution of hydrogen chloride is terminated, the product which, in the meantime



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has become very viscous, is heated to 150°C. with application of a very good vacuum and subsequently cooled. A colored, highly viscous mass is obtained which is partially soluble in hydrocarbons and which polymerizes when heated for a prolonged time, more rapidly after addition of peroxides. The polymers are non-combustible or self-extinguishing.

#### Example 14

276 Parts of glycerol (3 mols) and 301.5 parts of cyclohexanephosphonic acid dichloride (1.5 mols) are reacted under reduced pressure, first at 60°C. and then at 120°C. until the hydrogen chloride is completely eliminated. A device for separating water is installed. 299 parts of terephthalic acid (1.5 mols), 139 parts of fatty acid of linseed oil (0.5 mol) and 100 parts by volume of xylene are added and the mixture is heated under reflux. Within about 24 hours approximately 60 parts by volume of water can be drawn off. After having distilled off the xylene under reduced pressure and heated the product for about one hour at 170 to 180°C. there is obtained, after cooling, a highly viscous, yellow and completely clear product which does no longer flow. Baking tests with this material yield after 10 minutes at 200°C. on glass as well as on metal firmly adhering films having a good flow. Said films are not combustible.

#### Example 15

In a four-necked flask provided with a thermometer, stirring contrivance, and device for separating water with mounted reflux condenser there are heated to 180 to 190°C., while introducing nitrogen, 92 parts of glycerol (1 mol) and 192 parts of cyclohexylphosphonic acid dimethyl ester (1 mol) in the presence of 0.15% of CaO until the re-esterification is terminated. A yellow resin is obtained which is insoluble in water and which is not capable of flowing. The resin is well soluble inter alia in cyclic ethers, higher alcohols, halogenated hydrocarbons, esters, cyclohexanone and ethylene glycol monoethyl ether.

Solutions of said resin in one of the solvents mentioned above or mixtures thereof yield, when spread on sheet metal or glass and baked for 15 minutes at 200°C., films which have a good flow and a good hardness. Furthermore, the films are non-combustible.

#### Example 16

332 Parts of vinylphosphonic acid bis-*p*-chloroethyl ester (1 mol) and 62 parts of ethylene glycol (1 mol) are re-esterified as described in Example 15. A viscous resin is obtained which does not flow and which is capable of forming films when dissolved in a suitable solvent, for example butyl acetate or cyclohexanone.

#### Example 17

92 Parts of glycerol (1 mol) are re-esterified with 96 parts of cyclohexanephosphonic acid dimethyl ester (0.5 mol) as described in Example 15. After having cooled the resin to about 140°C. 58 parts of fumaric acid (0.5 mol) are added and the mass is heated to 180 to 195°C. in the presence of xylene as entrainer until the esterification is terminated. After having removed the xylene under reduced pressure, the resin is dissolved in ethylene glycol monoethyl ether. When said solution is spread, for example, on sheet metal there is obtained, after a baking period of 10 minutes at 200°C., a hard, clear and non-combustible film. When heat-

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ing to 80 to 100°C. the resin which is free of solvent, for example, in the presence of benzoyl peroxide, hard masses are obtained which do not burn or which are self-extinguishing.

#### Example 18

93 Parts of phenylphosphonic acid dimethyl ester (0.5 mol) are first re-esterified with 90 parts of butylene glycol (1 mol) as described in Example 17, and subsequently esterified with 49 parts of maleic anhydride (0.5 mol). A viscous resin is obtained which is no longer capable of flowing and which is soluble, for example, in halogenated hydrocarbons, esters, higher alcohols or in cyclic ethers; the resin can form films on glass or metals.

The resin which is free of solvent yields hard masses when heated for a short time to 80 to 100°C. in the presence of a polymerization initiator.

#### Example 19

In a manner analogous to that described in Example 17 there are re-esterified 152 parts of propylphosphonic acid dimethyl ester (1 mol), 62 parts of ethylene glycol (1 mol) and 69 parts of glycerol (0.75 mol) in the presence of 0.5% of sodium methylate. The mixture is subsequently esterified with 118 parts of succinic acid (1 mol). A yellow, viscous and non-flowing resin is obtained having good solubility properties and capable of forming films on glass and metal.

#### Example 20

50 Parts of fatty acid of linseed oil (0.18 mol) are heated for several hours to 170 to 200°C. with 96 parts of cyclohexanephosphonic acid dimethyl ester (0.5 mol) and 92 parts of glycerol (1 mol) in the presence of 1 part of CaO until the reaction is as complete as possible. After having cooled to about 140°C. there are added to the mixture 58 parts of fumaric acid (0.5 mol) and the water formed in the course of the esterification is removed by means of xylene as entrainer.

The esterification is carried out for several hours at 170 to 180°C. and is terminated when no more water distills off. After having distilled off the xylene under reduced pressure, a yellow, highly viscous, non-flowing resin is obtained which is soluble, among others, in cyclic ethers, ethyl glycol, esters of glycolic acid, halogenated hydrocarbons and phenols. When dissolved in a suitable solvent the resin furnishes, after a baking period of 10 minutes at 170°C., on glass and metal a very hard, elastic, firmly adhering and non-combustible film with a good flow.

#### Example 21

In the manner described in Example 20 there are re-esterified and esterified 50 parts of fatty acid of linseed oil (0.18 mol), 134 parts of hexane-triol (1 mol), 100 parts of benzylphosphonic acid dimethyl ester (0.5 mol) and 49 parts of maleic anhydride (0.5 mol). The resin dissolved in a suitable solvent bakes within 10 minutes at 170°C. and yields a very hard, well adhering and non-combustible film having a good flow.

#### Example 22

120 Parts of cyclohexanephosphonic acid d.a.y. ester (0.45 mol) are condensed with 110 parts of tricyclodecane-dimethylol and 20 parts (0.56 mol) of paratoluenesulfonic acid as described in Example 15. After having terminated the reaction an extremely viscous, slightly dark product is obtained which is well soluble in dioxane, higher alcohols and phenols.

## Example 23

134 Parts of hexane-triol (1 mol), 171 parts of cyclohexanephosphonic acid diallyl ester (0.7 mol) and 2 parts of CaO are heated together. After having distilled off the calculated amount of allyl alcohol, 127 parts of maleic anhydride (1.3 mols) and 90 parts of butanol (1.3 mols) are added. The water passing over in admixture with butanol is drawn off by means of a device for separating water which is filled to the overflow with butanol. After having terminated the condensation the reaction mixture is maintained for some time under reduced pressure. A dark, very viscous resin is obtained which, when dissolved in a suitable solvent, yields very good films on glass and metal.

The resin which is free of solvent is heated to 80 to 100°C., if desired in the presence of an initiator, to yield hard masses already after a short time.

## Example 24

184 Parts of glycerol (2 mols) are esterified at 160 to 180°C. with 148 parts of phthalic anhydride (1 mol). After cooling to about 140°C., there are added to the carboxylic acid polyester obtained 186 parts of phenylphosphonic acid dimethyl ester (1 mol) and 1 part of CaO and the whole mixture is heated to 180 to 190°C. until the re-esterification is complete. The resin thus obtained yields, when dissolved in a suitable solvent, a hard, elastic and non-combustible film on glass and metal after having been baked for 10 minutes at 170°C.

## Example 25

144 Parts of cyclohexanephosphonic acid dimethyl ester (0.75 mol) are reacted according to Example 20 with 146 parts of terephthalic acid dimethyl ester (0.75 mol), 140 parts of fatty acid of linseed oil (0.5 mol), 276 parts of glycerol (3 mols) and 174 parts of fumaric acid (1.5 mols). A yellowish resin is obtained which does no longer flow in the cold and which is well soluble in higher alcohols, cyclic ethers and phenols. When dissolved in a suitable solvent said resin yields, after having been baked for 10 minutes at 170°C., hard, elastic, firmly adhering and non-combustible films on glass and metal having very good flowing properties. The hardness and stability to solvents of said films can considerably be improved by the addition of 0.5 to 2.0% of a mineral acid, such as phosphoric acid and or perchloric acid.

## Example 26

60 Parts of a polyester prepared according to Example 9 from 212 parts of diethylene glycol, 195 parts of phenylphosphonic acid dichloride and 98 parts of maleic anhydride are dissolved in 40 parts of styrene. A clear, viscous mass is obtained which, after the addition of 0.5% of benzoyl peroxide at 60°C solidifies within a short time to form a light, transparent and very hard product.

## Example 27

70 Parts of a polyester obtained from 248 parts of ethylene glycol, 432 parts of maleic acid dimethyl ester and 195 parts of phenylphosphonic acid dichloride are admixed with 30 parts of styrene. The slightly yellowish product thus obtained is transformed with 0.5% of benzoyl peroxide at 70°C. within a few minutes into a completely transparent and very hard resin.

## Example 28

70 Parts of the same polyester as in Example 27 are mixed with 30 parts of vinyl toluene. After the addition of 0.5% of benzoyl peroxide the mixture hardens rapidly at 70°C. and yields a hard casting.

## Example 29

70 Parts of the same polyester as in Example 27 are mixed with 30 parts of diallyl terephthalate. 0.5% of benzoyl peroxide are then added to the resin whereupon it hardens at 70°C. to form a clear and solid product.

## Example 30

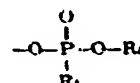
70 Parts of a polyester prepared from 96 parts of cyclohexylphosphonic acid dimethyl ester, 90 parts of butylene glycol and 49 parts of maleic anhydride are admixed with 30 parts of vinyl acetate. After the addition of 1% of para-toluene-sulfonic acid and 0.0003% of Cu-acetyl-acetonate there is obtained a hard product within a short time.

## Example 31

106 Parts of diethylene glycol are reacted according to Example 4 with 145 parts of vinyl-phosphonic acid dichloride. 70 Parts of the polyester thus obtained are mixed with 30 parts of styrene and after the addition of 0.3% of benzoyl peroxide the reaction product is transformed at 60°C. into a hard product.

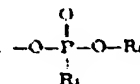
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. New polyesters containing a plurality of the group



wherein  $\text{R}_1$  stands for a member selected from the group consisting of monovalent alkyl, alkenyl, cycloalkyl, cyclo-alkenyl, aryl, aralkyl, alkylaryl radicals and halogen-, hydroxyl-, alkoxy substituted derivatives thereof and  $\text{R}_2$  is a bivalent radical of the group consisting of bivalent aliphatic, cycloaliphatic, aromatic hydrocarbon, polyglycol ether radicals and halogen-, hydroxyl- and alkoxy substituted derivatives thereof.

2. New polyesters containing a plurality of the group



wherein  $\text{R}_1$  stands for a member of the group consisting of monovalent aryl, aralkyl, alkyl-aryl radicals and halogen-, hydroxyl-, alkoxy-, amine, nitro substituted derivatives thereof and  $\text{R}_2$  is a bivalent radical of the group consisting of bivalent aliphatic, cycloaliphatic, araliphatic, aromatic hydrocarbon, polyglycol ether radicals and halogen-, hydroxyl- and alkoxy substituted derivatives thereof.

3. A process which comprises reacting at a temperature within the range of about 25-200°C., (A) a phosphonic acid derivative of the group consisting of the dihalides and the diesters of a phosphonic acid having an organic group of the glass consisting of monovalent alkyl, alkenyl, cycloalkyl, alkaryl groups and halogen-, hydroxyl- and alkoxy substituted derivatives thereof attached directly to the

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phosphorus atom of said phosphonic acid derivative with (B) at least 1 compound of the group consisting of saturated and unsaturated alcohols containing at least two free alcoholic hydroxyl groups.

4. A process according to Claim 3, wherein the phosphonic acid dihalide is a dichloride.

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5. A process according to Claim 3, wherein the reaction is carried out in the presence of at least one monohydric alcohol.